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(Commemoration Issue Dedicated to
Professor Waichiro Tsuji On the Occasion of
his Retirement)

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The Solubility and the Wet Spinning of Ethylene-Vinyl Alcohol Copolymers

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The solubility of ethylene-vinyl alcohol copolymer (EVA) and ethylene-vinyl alcohol-acrylic acid terpolymer (EVA-AA) in various solvents and the wet spinning of those were investigated in order to obtain fundamental information for preparing a new synthetic fiber that has high moisture regain, heat settability and stability in boiling-water.

The solvents for EVA and EVA-AA were organic solvents that act as a proton donor for the polymers such as phenol, m-cresol, formic acid and dimethyl sulfoxide and some mixed solvents such as n-propanol/ water and methanol/water mixture in a limited range.

The wet spinning of the both polymers in various conditions was examined. Besides the drawing and heat-treatment of the spun fibers, a cross-linking treatment was considered. It was found that the wet-spun fibers of EVA and EVA-AA have excellent mechanical properties as well as high moisture regain (4–13%) and low shrinkage (less than 7%) in boiling-water.

I. INTRODUCTION

Ethylene-vinyl alcohol copolymer (EVA) prepared from ethylene-vinyl acetate copolymer (EVAc) by saponification has a unique molecular character that the molecule is composed of typical hydrophobic and hydrophilic segments, ethylene (Et) and vinyl alcohol (VA) segments, respectively. Accordingly, its properties are expected to vary widely by its molecular composition. The relationship between the molecular composition and the crystalline structure or physical properties has been investigated on a series of the copolymers of different compositions by Matsumoto *et al.*^{1,2)} and Akabane *et al.*³⁾ It is found by those studies that the copolymers could be classified by the VA content into three groups that differ rather distinctly with each other in the crystalline structure. The copolymers in the first group with VA contents less than about 20 mol% exhibit a crystalline structure analogous to that of polyethylene(PE). The copolymers with VA contents of 20–60 mol% show an intermediate structure of PE and polyvinyl alcohol(PVA), and those with VA contents larger than 60 mol% indicate a crystalline structure analogous to that of PVA. It is also proved that the surface chemical property of EVA does not change monotonously according to the change of the composition but it varies rather abruptly at a specific composition. The hydrophobic property of the copolymers with smaller VA contents is abruptly lost at a VA content of 40 mol% and the hydrophilic property appears as the VA content increases.

However, there has been relatively little information on other properties of EVA. In this study the physical properties as a fiber material will be investigated.

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As a new material, EVA is a very interesting polymer as discussed above, and has many possibilities to be developed. EVA with low VA content is useful for hot-melt adhesive,⁴⁾ while EVA with high VA content will be useful as film and fibers because of its high oil resistance, non permeability of oxygen, high hygroscopic moisture regain and high crystallinity. There have been large numbers of patents granted for EVA as packing film material,⁵⁾ but very few for it as a material for synthetic fibers except du Pont patents⁶⁾ and as a blending material to viscose fiber.⁷⁾

As has been reported in a previous paper by the authors¹⁾ it has been shown that the melting point of EVA varies from that of PE, passing a minimum value (105°C) at around a VA content of 20 mol%, to that of PVA as the VA contents increase. Since the EVA with high VA contents gradually decomposes at the melting point, the melt spinning of it becomes very difficult. Accordingly its spinning process has to be achieved by wet or dry spinning. However, previous investigations on the solubility of EVA have reported only the solubility of EVA with VA contents of above 90 mol%.⁸⁾ An advanced study on the solubility of EVA is thus a very important subject in the course of developing EVA as the material of synthetic fibers. Wet spinning process of Nylon-6 fibers, though those are made by a melt-spinning at present, has been recently re-examined as the fiber properties may be improved by selecting the condition for the wet spinning.

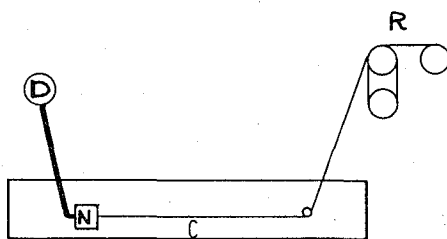
In view of the above facts, this study was undertaken for the purpose of developing a new synthetic fiber that has both hydrophilic and hydrophobic characteristics, utilizing the aforementioned peculiar properties of EVA. The solubility of EVA with high VA contents and EVA-AA in various solvents was mainly examined. Since EVA-AA has carboxylic acid groups, improved chemical reactivity, dyeing ability, and moisture regain were expected. Referring to the results obtained, a proper solvent for the wet-spinning was chosen and some properties of the fibers were studied.

II. EXPERIMENTAL

The copolymers used in this work are: (a) EVA (VA: 73.4 mol%, Et: 26.6 mol%) and (b) EVA-AA (VA: 59.4 mol%, Et: 34.6 mol%, AA: 6.0 mol%). The EVA-AA is a terpolymer containing acrylic acid, prepared by Nihon Gosei Chemical Industry Co., Ltd. The AA group is expected to give to the EVA improved chemical reactivity, dyeing capacity and moisture regain as mentioned in the introductory section. The degree of saponification of the both samples was more than 99.5 mol%. The other chemicals used in this work were a reagent grade.

The solubility of EVA and EVA-AA was determined by the following procedure: 50 mg. polymer and 1 ml. solvent were encapsuled in a glass tube and after heating at 200°C for an hour the transparency of the system was visibly observed at the chosen temperatures (30°C, 100°C, 150°C) to estimate the solubility. In order to investigate the dissolved state in a few solvents, the intrinsic viscosity $[\eta]$ was measured.

The fiber forming ability of the spinning dopes of the polymers prepared by a solvent decided above experiment into various coagulants, which is the most important factor in wet-spinning procedure, was examined by the following procedure. A drop of 20 wt% spinning dope was smeared on a glassplate and immersed into the coagulant. By this process a coagulant film was usually obtained. The coagulation process and the time re-



D : SPINNING DOPE
 N : NOZZLE
 R : ROLLER
 C : COAGULANT

Fig. 1. Apparatus for spinning.

quired for the coagulation were observed and the flexibility of the coagulated film was investigated. The result is shown in Table I, which will be discussed later.

The spinning apparatus used in this experiment is shown schematically in Fig. 1. The wet spinning was carried out using a nozzle with 0.3 mm diameter at various dope concentration, dope temperature and coagulation temperature. The stress-strain curve of fibers obtained was measured at 20°C, R. H. 65% by using AUTOGRAPH IM-100 (Shimazu Seisakusho Co., Ltd.) and the moisture regain was estimated from the weight increment at 30°C, R. H. 65%.

III. RESULTS AND DISCUSSION

III.1 Solubility of Ethylene-Vinyl Alcohol Copolymer and Ethylene-Vinyl Alcohol-Acrylic Acid Terpolymer

Hitherto to find out an adequate solvent for polymers the solubility parameter theory has been used. However, since this theory can be applied only to non-polar or poor polar polymers and no theory to polar polymers has been established, the solvent has been chosen only on experience. Generally speaking, there are two possible methods to find out a new solvent, namely: a method to select a solvent whose solubility parameter (δ) is the closest to the value for the polymer concerned and another to select a solvent that has a special interaction with the polymer. The latter case has been applied to polar polymers such as 3-Nylon,¹⁰ polyacrylonitril¹¹) and poly-L-proline.¹²) In this study, since EVA is composed of about 70 mol% VA and 30 mol% Et segments, it is expected that even if the copolymer has a high polarity there will be no appreciable amount of interaction with organic solvents because one molecule contains within itself hydrophobic as well as hydrophilic sequences.

The first step for the purpose is to study the solubility of various solvents, the solubility parameter of which differs in wide range.

In Table I, the δ value of the solvents and those solubility at 30, 100, and 150°C are shown. It is generally believe that the total solubility parameter is given by three factors, the dispersion force, polar force and hydrogen bonding force. The total solubility parameter (δ) can be written in the following equation:¹³)

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$

Table I. Solubility of Ethylene Vinyl Alcohol Copolymer at Various Temperature.

Solvent	Solubility parameter				30°C		100°C		150°C	
	δ	δ_d	δ_p	δ_h	EVA	EVA-AA	EVA	EVA-AA	EVA	EVA-AA
1 <i>n</i> -Hexane	7.24	7.24	0	0	I	I	I	I	I	I
2 Cyclohexane	8.18	8.18	0	0	I	I	I	I	I	I
3 Methyl isobutyl ketone	8.37	7.49	3.0	2.0	I	I	I	I	I	I
4 <i>n</i> -Butyl acetate	8.46	7.67	1.8	3.1	I	I	I	I	I	I
5 Carbon tetrachloride	8.65	8.65	0	0	I	I	I	I	I	I
6 Xylene	8.80	8.77	0.5	0.5	I	I	I	I	I	I
7 Toluene	8.91	8.82	0.7	1.0	I	I	I	I	I	I
8 Ethyl acetate	9.10	7.44	2.6	4.5	I	I	I	I	I	I
9 Benzene	9.15	8.95	0.5	1.0	I	I	I	I	I	I
10 Methyl acetate	9.15	7.6	3.5	3.7	I	I	I	I	I	I
11 Chloroform	9.21	8.65	1.5	2.8	I	I	I	I	I	I
12 Methyl ethyl ketone	9.27	7.77	4.4	2.5	I	I	I	I	I	I
13 Trichloroethylene	9.28	8.78	1.5	2.6	I	I	I	I	I	I
14 Tetrahydrofuran	9.52	8.22	2.8	3.9	I	I	I	I	I	I
15 Chlorobenzene	9.57	9.28	2.1	1.0	I	I	I	I	I	I
16 Methylene chloride	9.76	8.91	3.1	3.0	I	I	I	I	I	I
17 Acetone	9.77	7.58	5.1	3.4	I	I	I	I	I	I
18 Cyclohexanone	9.88	8.65	4.1	2.5	I	I	I	I	I	I
19 Dichlorobenzene	9.98	9.35	3.1	1.6	I	I	I	I	I	I
20 Dioxane	10.0	9.30	0.9	3.6	I	I	I	I	I	I
21 Tetrachloro ethane	10.56	9.20	2.5	4.6	I	I	I	I	I	I
22 <i>tert</i> -Butanol	10.6				I	I	I	I	I	I
23 Pyridine	10.6	9.25	4.3	2.9	I	I	I	I	P	I
24 <i>sec</i> -Butanol	10.8				I	I	I	I	I	I
25 Cyclohexanol	10.95	8.50	2.0	6.6	I	I	I	I	I	I
26 <i>iso</i> -Butanol	11.1	7.4	2.8	6.3	I	I	I	I	I	I
27 <i>m</i> -Cresol	11.1	8.82	2.5	6.3	S	S	S	S	S	S
28 <i>n</i> -Butanol	11.3	7.81	2.8	7.7	I	I	I	I	I	I
29 <i>iso</i> -Propanol	11.5	7.70	3.0	8.0	I	I	I	I	I	I
30 Phenol	11.8	8.8	2.9	7.3	S	S	S	S	S	S
31 <i>n</i> -Propanol	11.97	7.75	3.3	8.5	I	I	I	I	I	I
32 Benzylalcohol	12.1				I	I	I	I	I	I
33 Dimethyl formamide	12.14	8.50	6.7	5.5	I	P	S	S	S	S
34 Formic acid	12.15	7.0	5.8	8.1	S	S	S	S	S	S
35 Ethylene chlorohydrin	12.2				S	I	S	I	S	S
36 Nitromethane	12.3	7.70	9.2	2.5	I	I	I	I	I	I
37 Ethanol	12.9	7.73	4.3	9.5	I	I	I	I	P	I
38 Dimethyl sulfoxide	12.93	9.00	8.0	5.0	S	S	S	S	S	S
39 Methanol	14.28	7.42	6.0	10.9	I	I	I	I	I	I
40 Propylene glycol	14.80	8.24	4.6	11.4	I	I	P	I	P	S
41 Ethylene glycol	16.3	8.25	5.4	12.7	I	I	P	I	S	S
42 Formamide	17.8	8.40	12.8	9.3	I	I	P	I	S	S
43 Glycerol	21.1	8.46	5.9	14.3	I	I	P	I	P	P
44 Water	23.5	6.0	15.3	16.7	I	I	P	I	P	I

S: Soluble

P: Partially soluble

I: Insoluble

δ_d , δ_p , and δ_h represent the effects of dispersion, polar and hydrogen bonding forces, respectively. In Table I, solvents are arranged according to the polarity. Based on these results, together with our previous study¹⁴ on the solubility of EVA with a low VA content, it is clear that with increasing of VA content EVA and EVA-AA become to be soluble into solvent with higher value of δ , especially higher δ_h . The difference in the solubility between EVA and EVA-AA could be hardly detected. From the above results, it may be concluded that, even if EVA-AA contains a VA content of 59.4 mol%, 14 mol% lower than that of EVA, the over all polarity of EVA-AA is nearly equal to that of EVA due to the AA content of 6 mol% in the terpolymer. It is noticed that with rising of the temperature, the solubility of EVA and EVA-AA in high δ_p solvents increases comparing with that in high δ_h solvents because of the heat scission of hydrogen bond.

Next, we studied the solubility in alcohol/water mixed solvents. Figure 2 shows the solubility of copolymers. It can be seen that EVA has a solubility in a wide range of composition of the n-propanol/water mixture, but only in a limited range of composition for methanol/water mixture. It may be considered from this phenomenon that the polarity and the chemical structure of EVA are very similar to those of n-propanol/water mixture. On the other hand, EVA-AA was dissolved in methanol/water mixed solvent in a wider range of composition than EVA. The composition of the mixed solvent at the

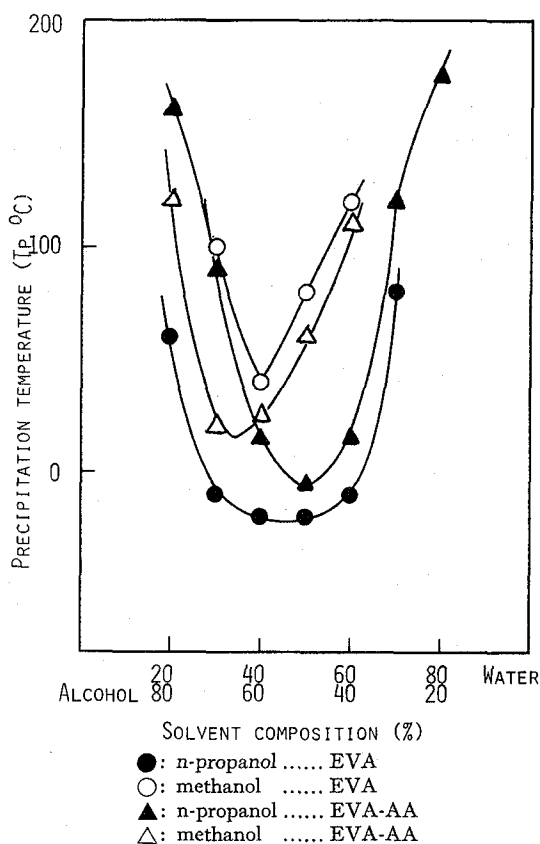


Fig. 2. Relationship between solvent composition and precipitation temperature of EVA and EVA-AA.

Table II. Solubility of Solvents.

Solvents	EVA		EVA-AA	
	$[\eta]$	k'	$[\eta]$	k'
Dimethyl sulfoxide	0.66	0.32	0.62	0.33
n-Propanol/water (6/4 vol. ratio)	0.65	0.24	0.59	0.39
Phenol/water (7.5/2.5 vol. ratio)	0.94	0.35	0.76	0.59

Intrinsic viscosity $[\eta]$ and Huggins' constant k' were measured at 30°C

minimum of precipitation temperature for EVA-AA was 7/3 vol. ratio in methanol/water while that of EVA was 6/4 vol. ratio. This difference in solubility will come from the difference in the polarity and chemical structure of the copolymers. Further, the table shows that the solvents of EVA and EVA-AA have the same character; those δ are ranged from 11 to 13 and those are strong proton donors.

It may be concluded from these results that the solvents of EVA and EVA-AA are dimethyl sulfoxide, m-Cresol, Formic acid, n-propanol/water, methanol/water and phenol/water. In order to clarify the dissolved state in these solvents, intrinsic viscosities $[\eta]$ at 30°C were measured.

Table II shows the $[\eta]$ and Huggins' k' . $[\eta]$ of EVA in phenol/water (7.5/2.5, vol. ratio) is the highest. Accordingly the phenol/water mixture is a good solvent. In case of EVA-AA, the phenol/water mixture is not so good solvent because it has a large value of k' . There are little difference in solubility between dimethyl sulfoxide and n-propanol/water mixture.

The wet spinning of the copolymers with use of various solvents tested here was next examined to improve fiber properties. In this study, the spinning dopes were prepared by dimethyl sulfoxide, n-propanol/water, methanol/water as its solvents. The wet spinning was carried out varying dope concentration and spinning temperature.

III.2 Coagulating Properties of Various Coagulants for Spinning Dopes

The coagulation ability was preliminary investigated at 20 wt% dope concentration, 30°C dope temperature and 15°C coagulant bath temperature.

Table III shows some of the results. The coagulation ability of the aqueous solution of various salts for EVA and EVA-AA was investigated referring to the wet spinning of PVA. We will first discuss the result of EVA. In case of n-propanol/water solution, most of the coagulants could not enough coagulate the dope and it tended to spread over the surface of coagulant. Whereas, in case of dimethyl sulfoxide solution, most of the coagulants sufficiently coagulated the spinning dope. There were some differences among the coagulating abilities of various coagulants. It was found that pure water was the best coagulant.

As for the EVA-AA terpolymer, the methanol/water dope did not spread over the coagulant surface except in the case of some coagulants and the dope had better fiber forming ability than the n-propanol/water dope and was coagulated easily with pure water.

From these results, dimethyl sulfoxide dope was chosen as the spinning dopes of EVA and EVA-AA. The wet spinning was carried out as follows.

Solubility and Spinning of Ethylene-Vinyl Alcohol Copolymers

Table III. Coagulation Properties of EVA and EVA-AA Spinning Dope Using n-Propanol/Water, Dimethyl Sulfoxide, and Methanol/Water as its Solvent.

Cogulant		EVA		EVA-AA	
Solute	Concn. of aq. soln. (wt%)	n-Propanol/water (7/3 vol. ratio)	Dimethyl sulfoxide	Methanol/water (7/3 vol. ratio)	Dimethyl sulfoxide
H ₂ O		×	○	○	○
H ₂ SO ₄	20	×	○	△	○
(NH ₄) ₂ SO ₄	20	×	△	△	△
Na ₂ SO ₄	sat.	×	×	○	○
ZnSO ₄	20	×	△	○	○
FeSO ₄	sat.	×	△	△	△
MgSO ₄	20	×	△	△	△
CuSO ₄	20	△	○	○	○
CaSO ₄	sat.	△	○	△	○
Al ₂ (SO ₄) ₃	sat.	×	×	△	○
NH ₄ NO ₃	20	×	○	△	○
NaNO ₃	20	×	○	△	○
Mn(NO ₃) ₂	20	×	○	×	△
CH ₃ COOH	20	×	×	△	△
NH ₄ OCOCH ₃	20	×	△	○	△
NaOCOCH ₃	20	×	△	○	○
Ca(OCOCH ₃) ₂	20	×	×	×	○
Mg(OCOCH ₃) ₂	20	×	×	×	△
Pb(OCOCH ₃) ₂	20	×	×	△	○
Zn(OCOCH ₃) ₂	20	×	×	×	△
Cr(OCOCH ₃) ₃	20	×	△	○	△
NaCl	20	×	△	△	×
(NH ₄) ₃ PO ₄	20	×	○	×	×
K ₂ CrO ₄	20	×	△	×	△
K ₂ Cr ₂ O ₇	sat.	△	○	△	○
NH ₄ OH	20	×	△	△	×
KOH	20	×	×	×	×
NaOH	20	×	×	△	△
Mg(OH) ₂	sat.	×	○	○	○
Zn(OH) ₂	sat.	△	○	△	○
Cu(OH) ₂	sat.	△	○	○	○
Ca(OH) ₂	sat.	×	○	△	○
Al(OH) ₃	sat.	△	○	○	○

○: homogeneous, flexible.

△: non-homogeneous, inflexible.

×: spread over the coagulant, non-film forming.

III. 3 Wet Spinning and Fiber Properties

The spinning apparatus used in this work is shown schematically in Fig. 1. The temperature and dope concentration were closely related with the coagulation speed, viscosity of dope and the fiber forming ability. From a pre-experiment, main spinning conditions were decided as follows;

Nozzle	mono-hole of 0.3 mm diameter
Length of coagulation bath	1.5 m
Winding speed	1-4 m/min. varied according to coagulation speed
Concentration of dope	10-30 wt% dimethyl sulfoxide soln.
Temperature of dope	50°C
Coagulation bath temperature	15°C

Figure 3 shows the relationships between the maximum draw ratio and temperature for the fibers obtained by above spinning conditions. With increasing of the dope concentration of EVA and EVA-AA, the temperature giving a maximum draw ratio rises a little, and the maximum draw ratio decreases. The optimum temperature (130°C) for the drawing of EVA-AA is a little higher than that of EVA (120°C) and the maximum draw ratio decreased from 8 times to 6 times. This may be brought about by the increase in the polarity. In order to obtain good fiber properties, especially good mechanical properties it is necessary to increase the draw ratio. It was decided that the fiber specimens were drawn 6 times at 120°C for EVA and 5 times at 130°C for EVA-AA.

Table IV shows some fiber properties of EVA and EVA-AA. When the dope concentration of EVA was 10 wt% and 15 wt%, the dope viscosity was too small to carry out the wet spinning. On the other hand, for the EVA-AA dope above 25 wt%, the dope viscosity was too high to perform the wet spinning. These difference in viscosity was resulted from the difference in degree of polymerization and the existence of acrylic acid segment in EVA-AA.

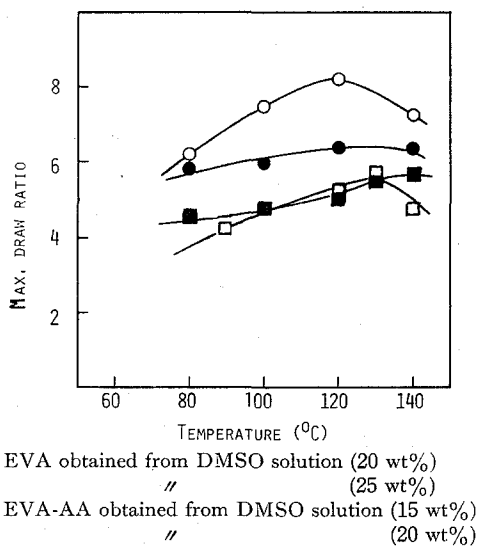


Fig. 3. Relationship between maximum draw ratio and drawing temperature.

Table IV. Mechanical Properties, Moisture Regain and Heat Settability of EVA and EVA-AA Fiber.

Polymer	Fiber		Dry			Wet			Moisture regain for 8 hrs at 30°C, 65% R.H. (%)	Heat settability (%)
	Dope conc. (wt%)	Heat treatment temp. (°C)	Tensile strength (g/d)	Elongation at break (%)	Young's modulus (g/d)	Tensile strength (g/d)	Elongation at break (%)	Young's modulus (g/d)		
EVA	20	170	4.1	17	64.9	4.2	20	50.1	3.9	97.3
	20	180	3.9	15	63.0	4.0	20	52.3	3.2	94.2
	25	160	4.7	16	69.8	4.5	22	53.1	3.3	95.6
	25	170	4.2	21	56.8	4.3	19	50.2	3.3	82.2
	25	180	4.8	18	69.6	5.2	20	44.1	3.1	96.7
	30	160	4.7	14	66.1	3.8	21	43.4	3.0	97.7
	30	170	4.5	19	54.1	4.2	22	53.1	3.1	93.6
	30	180	4.0	18	55.6	4.1	21	49.5	2.9	96.1
EVA cross-linked by pyromeric acid		180	3.8	22	55.7	3.9	21	50.3	1.6	94.7
EVA-AA	10	150	2.4	33	41.5	1.7	32	16.0	6.8	97.4
	15	150	3.3	21	45.3	1.8	29	22.0	5.3	95.3
	20	150	3.4	24	43.1	2.3	26	28.0	4.8	97.4
EVA-AA cross-linked by ethylene diamine		170	2.3	70	36.5	1.3	84	19.5	8.7	99.7
		175	3.3	26	39.0	1.4	34	13.9	9.3	99.4
		180	2.3	23	33.9	1.0	40	13.5	8.6	98.6
Nylon 6			6.4	48	22.0	6.7	49	23.0	3.9	75.2
Vinylon (degree of formalization 24%)			3.7	11	45.0	3.2	13	37.0	4.3	65.6

The hygroscopic properties which is the most important factor for textile fiber can be discussed with the data in Table IV. In this Table, moisture regains at 30°C, R. H. 65%, for 8 hours are indicated in percentage. The equilibrium moisture regains are shown in Fig. 5. In all fibers, with increasing of dope concentration, the moisture regain of fiber decreases. It may be due to the fact that the higher the dope concentration, the less the formation of microvoids, and its fine structure was maintained after the drawing and heat treatment. Moreover, with increasing of the temperature of heat treatment, the moisture regain of fiber decreases probably due to the decreasing of free OH groups that act as adsorption sites.

The moisture regain of these EVA fibers about 4% is smaller than that of cotton (about 8%), but it is nearly equal to that of Nylon 6 and normal Vinylon fiber. On the other, even if the fiber of EVA-AA contains a VA content of 59.4 mol%, 14 mol% lower than that of EVA, the moisture regain is about 7% owing to the existence of hydrophilic AA groups of 6 mol%. The AA groups might remarkably affect on the crystallinity and crystal structure of the polymer. From the X-ray diffraction pattern, the crystallinity and the crystal structure of EVA-AA were determined. The result will be reported elsewhere. In Fig. 4, the X-ray diffraction patterns of the drawn EVA and EVA-AA are shown, which reveal a high degree of molecular orientation. It is clear that most of AA groups locate in the amorphous region and, therefore, the moisture regain and dyeing ability are maintained even by the heat treatment. The degree of crystallinity of the EVA-AA fiber is about 25%. On the contrary, the EVA fiber has a degree of crystallinity of 45%. This may be one of the reasons for the large moisture regain of the EVA-AA fiber. However, the EVA-AA fiber has a poor stability in hot-water and breaks at 84°C as shown in Fig. 6 which will be described later. In order to improve the stability in hot-water, cross-linking of the EVA-AA fiber by ethylene diamine was investigated. The moisture regain of the EVA-AA fiber increases to about 9% by the cross-linking as indicated in Table IV.

Figure 5 shows the relationship between adsorption time and moisture regain of various fibers. The initial moisture regain of EVA and EVA-AA fibers is lower than that of Nylon 6 and Vinylon. This is due to the large denier of the present fibers (about 60 d)

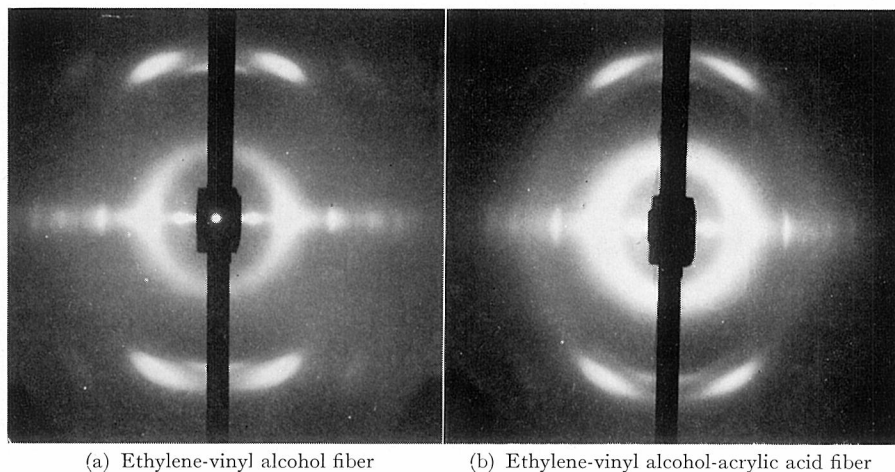


Fig. 4. X-ray diffraction pattern of drawn ethylene-vinyl alcohol fiber and ethylene-vinyl alcohol-acrylic acid fiber.

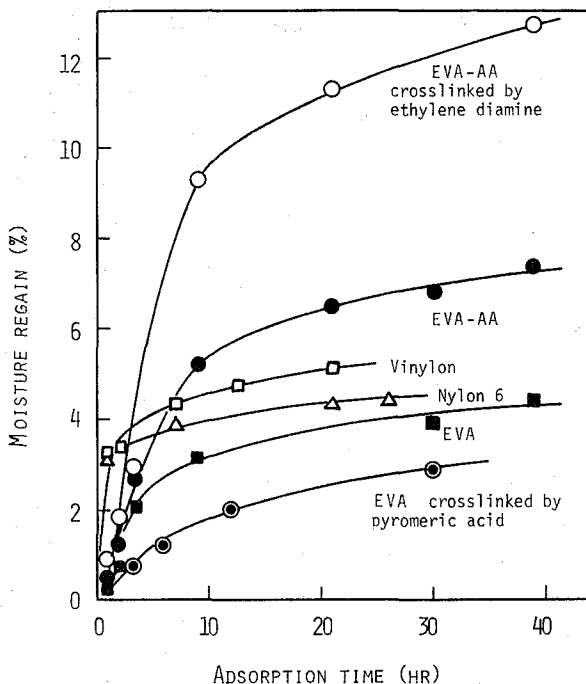


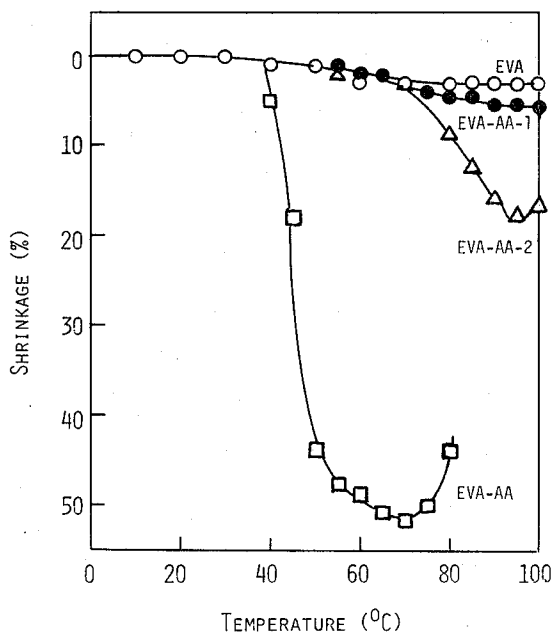
Fig. 5. Adsorption time dependence of moisture regain of various fibers.

(○) EVA-AA cross-linked by ethylene diamine, (●) EVA-AA, (□) Vinylon, (△) Nylon 6, (■) EVA, (⊙) EVA cross-linked by pyromeric acid

as compared with Nylon 6 (5 d) and Vinylon (2 d). It is evident from Fig. 5, that the equilibrium values of moisture regain of the EVA, EVA-AA and cross-linked EVA-AA fibers are 4.5%, 7.5%, and 13%, respectively.

The mechanical properties of these fibers are shown in Table IV. The tensile strength and elongation at the break and the Young's modulus of the EVA fiber are 4–5 g/d, 15–20% and 55–70 g/d, respectively, while those of the EVA-AA fiber and the cross-linked EVA-AA fiber are 2.5–3.5 g/d, 20–30%, 30–45 g/d, and 2 g/d, 45%, 20–30 g/d, respectively. The Young's moduli of these fibers are higher than that of Nylon fiber and comparable to that of Vinylon. However, at the wet state these properties particularly, Young's modulus of the EVA-AA and the cross-linked EVA-AA fibers slightly deteriorate because of its lower crystallinity and high hygroscopicity. Figure 6 shows the stability in hot-water. When the EVA fiber was sufficiently heat-treated at 180°C, the stability in hot-water, *e.g.* the shrinkage in hot-water was less than 5%. Since the mechanical properties of the EVA and the EVA-AA fiber are supported by the crystallites in the structure, the decrease in the degree of crystallinity improves the moisture regain but deteriorates the mechanical properties of fibers. The EVA-AA fiber having a low crystallinity and having AA group as an adsorption site has a poor stability in hot-water and breaks at 84°C as shown in Fig. 6.

In order to improve this stability, the cross-linking was introduced into EVA-AA by ethylene diamine. It is obvious from Fig. 6 that with rising of the temperature for the treatment, with rising the cross-linking density, the shrinkage in hot-water is decreased. For example, if the cross-linking reaction was made after the drawing and heat set for the EVA-AA fibers by dipping into 5% methanol solution of ethylene diamine at 50°C for 30



EVA-AA: Draw and heat set at 130°C
 EVA-AA-1: Cross-linked by ethylene diamine 5 wt% methanol soln. dipping time 30 min. at 50°C. re-heat set at 180°C
 EVA-AA-2: Cross-linked by ethylene diamine 5 wt% methanol soln. dipping time 5 min. at 50°C re-heat set at 180°

Fig. 6 Water stability of various fibers.

min. and re-heating at 180°C for 5 min. while holding the fiber length, the shrinkage of the fibers became as small as 7%.

It is concluded from the results of this investigation that a new synthetic fiber which has characteristically very high moisture regain, good stability in hot-water and high heat settability may be obtained from the EVA and EVA-AA polymers.

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